

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE March 28, 1996	3. REPORT TYPE AND DATES COVERED Technical Report #31		
4. TITLE AND SUBTITLE Photoinduced Orientation and Some of Its Photonic Consequences in Amorphous Azo-Containing Polymers		5. FUNDING NUMBERS N00014-93-1-0615		
6. AUTHOR(S) A. Natansohn and P. Rochon		8. PERFORMING ORGANIZATION REPORT NUMBER 31		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Queen's University Kingston, Ontario K7L 3N6 Canada		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of the Naval Research 800 North Quincy Street, Arlington, VA 22217-5000		11. SUPPLEMENTARY NOTES Submitted to Polymer Materials: Science and Engineering Division Preprints (ACS)		
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Photoinduced birefringence, surface gratings inscription and two-beam coupling properties are investigated on a series of amorphous high-Tg azo-containing polymers. For photoinduced birefringence, a neighboring group effect was observed, and dipolar interaction is demonstrated to be the main factor determining cooperative motion of side groups below Tg. Surface gratings can act as optical couplers into waveguides on the polymer films. Asymmetrical (photorefractive) and two-beam coupling due to multiwave mixing can be exploited for switching elements. In principle, a whole photonic device can be envisaged on a simple polymer film and obtained by optical inscription.				
14. SUBJECT TERMS Azo polymers, photonic devices, photoinduced birefringence, two-beam coupling		15. NUMBER OF PAGES 1		
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		16. PRICE CODE
19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT unlimited		

19960412 080

OFFICE OF NAVAL RESEARCH

GRANT: N00014-93-1-0615

R&T CODE: 3132081

Scientific Officer: Dr. Kenneth J. Wynne

TECHNICAL REPORT NO. 31

**Photoinduced Orientation and Some of Its Photonic Consequences in
Amorphous Azo-Containing Polymers**

by

A. Natansohn and P. Rochon

**Submitted for publication
in**

Polymer Materials: Science and Engineering Division Preprints (ACS)

**Department of Chemistry
Queen's University
Kingston, On., Canada**

March 28, 1996

**Reproduction in whole or in part is permitted for any purpose of the
United States Government**

**This document has been approved for public release and sale;
its distribution is unlimited.**

PHOTOINDUCED ORIENTATION AND SOME OF ITS PHOTONIC
CONSEQUENCES IN AMORPHOUS AZO-CONTAINING POLYMERS. A.
Natansohn¹ and P. Rochon², ¹Department of Chemistry, Queen's University,
Kingston, Ont. K7L 3N6 and ²Department of Physics, Royal Military College,
Kingston, Ont. K7K 5L0, Canada

Photoinduced birefringence, surface gratings inscription and two-beam coupling properties are investigated on a series of amorphous high-Tg azo-containing polymers. For photoinduced birefringence, a neighboring group effect was observed, and dipolar interaction is demonstrated to be the main factor determining cooperative motion of side groups below Tg. Surface gratings can act as optical couplers into waveguides on the polymer films. Asymmetrical (photorefractive) and two-beam coupling due to multiwave mixing can be exploited for switching elements. In principle, a whole photonic device can be envisaged on a simple polymer film and obtained by optical inscription.

ABSTRACT. Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.

☐ A. DIVISION OF Polymeric Materials: Science and Engineering

☐ B. MEMBER ☒ Yes ☐ No

☐ C. TITLE OF PAPER Photoinduced Orientation and some of its
Photonic Consequences in Amorphous
Azo-Containing Polymers.

(To be filled in by Division)

Paper number as listed on program _____

☐ E. Principal Author's Business Mailing
Address Including Zip Code
Dr. A. Natansohn
Department of Chemistry
Queen's University
Kingston, Ontario K7L 3N6
Canada

Please indicate preference: X oral _____ poster (invited)

☐ D. AUTHORS

Principal Author:

Surname	First Name	MI
NATANSOHN	ALMERIA	L

Presenting Author (if different)

Co-authors:

PAUL ROCHON

☐ F. Principal Author's Telephone, Fax
Number, and E-mail Address

613-545-2008 (phone)
613-545-6669 (fax)
natansoh@chem.queensu.ca

☐ G. For contributed papers, do authors
meet criteria outlined in ACS Bylaw
VI, Section 6(3)? See instructions.

☐ Yes ☐ No

**NOTE: ALL PRESENTING AUTHORS MUST REGISTER FOR THE MEETING—EITHER FULL MEETING
REGISTRATION OR ONE-DAY REGISTRATION FOR THE DAY OF PRESENTATION.**

☐ H. Specify Equipment Required for Presentation Other than 2" x 2" (35MM) slide or overhead (transparency) projector

PHOTOINDUCED ORIENTATION AND SOME OF ITS PHOTONIC CONSEQUENCES IN AMORPHOUS AZO-CONTAINING POLYMERS

Almeria Natansohn¹ and Paul Rochon²

¹Department of Chemistry, Queen's University, Kingston, Ontario, K7L

3N6 ²Department of Physics, Royal Military College, Kingston, Ontario, K7K 5L0, CANADA

Three different properties are of interest in the study of azo-containing polymers in our laboratory:

Photoinduced Birefringence

In the process of photoinducing orientation in amorphous azo-containing polymers, we have identified a few structural factors affecting the level and the rate of inducing birefringence. The most interesting factor is a neighboring groups effect, which favors cooperative motion of azobenzene groups bound on the same polymer chain¹⁻³. Since this effect is evidenced for the first time in amorphous polymers, we were interested in determining if the driving force was steric (as is the case in liquid crystalline polymers, where the rigid groups move in concert due mainly to their similar shape) or dipolar. A dipolar driving force would arise from the electric field of the neighboring rigid dipoles. Experimental evidence up to date strongly suggests that the driving force is dipolar. A rigid group of similar shape and polarity (a substituted phenyl benzoate ester, for example)³ moves in concert with the azobenzene group when the latter is moved by polarized light. If the same group (same size, same shape) has a much smaller dipole moment ("non-substituted" phenyl benzoate)⁴, no cooperative motion is observed.

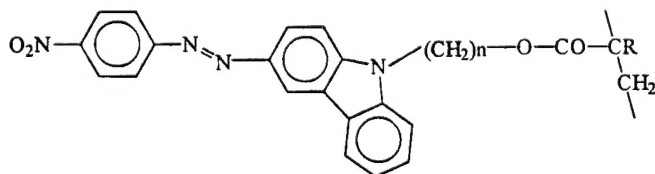
In-situ orientation studies performed by monitoring infrared dichroism while birefringence was being photoinduced, clearly show different motions of the azobenzene and of the phenyl benzoate groups⁵.

Surface gratings

Deep periodic surface gratings can be inscribed on azobenzene-containing polymer films by interfering beams, thus giving the possibility for long-term holographic storage^{6,7}. The mechanism of inscribing such gratings was proposed to be pressure-driven⁸ and will be described in a separate paper in this symposium⁹.

Two-beam coupling

A third property of some of the amorphous, high-T_g, azobenzene-containing polymer films is the ability for two-beam coupling, symmetric and asymmetric. Symmetric two-beam coupling can be obtained after inscription of a volume grating on the film (exploiting differences in birefringence) or of a surface grating, as mentioned above. Either grating will diffract incoming beams and may produce gain or loss¹⁰. Asymmetric coupling can be obtained by exploiting the inherent photorefractive properties of at least some of these polymers^{10,11}. An example of a class of polymers studied for its photorefractive properties is presented below:



These polymers contain the rigid polar azobenzene groups which can be poled in the presence of an electric field. Such an arrangement has electro-optic activity. The presence of the amino group provides

photoconductive properties, and in the case presented above, carbazole is a well-known photoconductive group in various polymer structures. When the combination of electro-optic activity and photoconductivity is present in a polymer, photorefractivity is a possibility¹². Photorefractivity has been demonstrated in the visible ($\lambda = 534$ nm) for thin films of the polymer with $n = 2$ by performing asymmetric two-beam coupling¹⁰, which is a definitive test for photorefractivity¹³. By performing photoinduced poling with two interfering laser beams, birefringence gratings and surface gratings are also created in the polymer film, and the consequence is the appearance of two-beam coupling other than that produced by photorefractivity. Two-beam coupling due to multiwave mixing can be observed in the absence of an electric field. Thus, this third property is fairly complex and more research is required before it can be used for optical switching.

Potential for devices

Stable birefringence can be locally induced and erased on a polymer film made of an azobenzene-containing polymer at a very high resolution. The birefringence can be used as a memory bit, or can be used for waveguide purposes. A "printed circuit" of waveguides can in principle be drawn on such a polymer film. At the points of incidence with a light beam coming from outside the film, the surface grating can be used to couple the external beam into and out of the polymer film. Such a surface grating can be obtained by exclusive optical means and its efficiency and direction of guiding are adjustable. Such a grating can also be erased, although local heating would be required for erasing. Finally, by local poling on films with photorefractive properties, or by exploiting symmetrical two-beam coupling, optical switches can be obtained. In principle, such an integrated circuit can be changed at will using only optical means.

Acknowledgments

Funding for this project is provided by the Office of Naval Research, NSERC Canada and the Department of Defence, Canada. The contributions of all our postdoctoral associates (M. S. Ho, X. Meng) and graduate students (S. Xie, C. Barrett, D. Brown, J. Paterson, S. To) were essential in developing this project. A. N. thanks Canada Council for a Killam Research Fellowship.

References

1. D. Brown, A. Natansohn and P. Rochon, *Macromolecules*, **28**, 6116 (1995).
2. M. S. Ho, A. Natansohn and P. Rochon, *Macromolecules*, **29**, 44 (1996).
3. X. Meng, A. Natansohn, C. Barrett and P. Rochon, *Macromolecules*, **29**, 946 (1996).
4. X. Meng, A. Natansohn, C. Barrett and P. Rochon, *Polym. Prepr. (ACS)*, **37**(1), 127 (1996).
5. M. Pézolet and T. Buffeteau, in preparation.
6. P. Rochon, E. Batalla and A. Natansohn, *Appl. Phys. Lett.*, **66**, 136 (1995).
7. D. Y. Kim, S. K. Tripathy, L. Li and J. Kumar, *Appl. Phys. Lett.*, **66**, 1166 (1995).
8. C. Barrett, A. Natansohn and P. Rochon, *J. Phys. Chem.*, in press.
9. C. Barrett, A. Natansohn and P. Rochon, *Polym. Mater. Sci. Eng.*, submitted.
10. M. S. Ho, C. Barrett, J. Paterson, M. Esteghamatian, A. Natansohn and P. Rochon, *Macromolecules*, submitted.
11. M. S. Ho, C. Barrett, P. Rochon and A. Natansohn, in *Organic Thin Films for Photonic Applications*, OSA Technical Digest Series, **21**, 338 (1995).
12. W. E. Moerner and S. M. Silence, *Chem. Rev.*, **94**, 127 (1994).
13. L. Yu, W. K. Chan, Z. Peng and A. Gharavi, *Acc. Chem. Res.*, **29**, 13 (1996).